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**54 PROCESS FOR THE PRODUCTION OF MAGNETIC POLYMER PARTICLES.**

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## Description

The present invention relates to a process for the preparation of magnetic polymer particles. It has been tried to use magnetic polymer particles within several fields of biochemistry and medicine. They have been tried as carriers for pharmaceutical preparations since they due to their magnetic properties are capable of transporting the preparations to the desired location in the body. Magnetic particles also have other practical applications and have been used within diagnostics since it is possible to replace separation of particles by means of centrifugation by the much simpler method of magnetic extraction. Further, magnetic particles have been used for cell separation and as carriers for enzymes. Of more technical applications may be mentioned toners for copying purposes.

Previous processes for preparing particles containing for instance magnetic iron oxide (magnetite) have started from magnetite  $\text{Fe}_3\text{O}_4$ . In several ways it has been tried to coat the magnetite particles with polymeric material to obtain polymer particles containing magnetite.

A commonly used method employs magnetite powder which is mixed mechanically with molten polymer. After this treatment the polymeric material containing magnetite is finely divided. This provides particles having an uneven shape and being of different size. Particles prepared in this manner are often used as toner, but the uneven shape is undesired since it will result in uneven and unsharp edges on the characters.

Another method employs finely divided magnetite to which vinyl monomer and initiator are added in water to form polymer around the magnetite grains. This will also provide magnetic particles having an undefined and highly variable size and shape. Further, only some of the particles will be magnetic, and the content of magnetite in the particles is usually very unequal. Other methods describe admixture of albumin and other proteins with magnetite and vigorous stirring in water with emulsifier to form drops which contain magnetite and protein. Another method comprises treatment of swelling polymer particles with finely divided magnetite to obtain magnetite on and possibly some inside the particles.

The fact that magnetite is used will, even if it is employed in very finely divided form, represent great limitations with respect to the type and the size of the particles. A real diffusion of molecular material into the particles or into pores of the particles will not take place. With solid, porous particles very large pores would be necessary, and accordingly large particles, so that magnetite grains are deposited not only on the surface of the particles. With highly swelling particles it is possible to get some magnetite into the particles mechanically, but the magnetite will essentially be deposited on the surface and result in a very uneven surface.

According to the process of the present invention iron is introduced into the particles in the form of salts and is then converted to magnetic iron oxide which to a great extent will be magnetite ( $\text{Fe}_3\text{O}_4$ ) or oxides having corresponding magnetism.

For many of the above purposes, the particles prepared according to the invention will be advantageous since they are spherical and have an even concentration of magnetic material which may be varied as desired within wide limits. In particular, the process provides the possibility for preparing monodisperse particles of desired size, compact as well as porous.

The process according to the present invention is suitable for compact as well as porous polymer particles and may be used for the preparation of magnetic polymer particles of all sizes. In particular the process is suitable for the preparation of particles in the range  $0.5\text{--}20\text{ }\mu\text{m}$ , but it may also be used for the preparation of particles smaller than  $0.5\text{ }\mu\text{m}$  and larger than  $20\text{ }\mu\text{m}$  in diameter. A great advantage of the process is that it allows all the particles to have the same concentration of magnetic iron oxide. When monodisperse polymer particles are used as starting material, the process will in particular provide monodisperse magnetic polymer particles which all contain the same amount of magnetic iron oxide.

According to the invention there is provided a process for preparing magnetic polymer particles. The process is characterized in that solutions of iron salts and optionally salts of other metals which are capable of forming magnetic ferrites, in water or in a mixture of water and water-soluble organic solvents or in organic solvents, are mixed with polymer particles in dry form or dispersed in water or in a mixture of water and water-soluble organic liquids or in organic liquids, and the metals are precipitated in the form of hydroxides and, optionally, the particles are heated. The precipitation may be carried out by raising the pH.

In the following description of the new process for the preparation of magnetic polymer particles, the preparation of magnetic particles containing magnetite  $\text{Fe}_3\text{O}_4$ , which may also be described as ferroferrite,  $\text{FeFe}_2\text{O}_4$ , is described in detail.

As it will be seen, it is also possible to use some of the described embodiments for the preparation of polymer particles containing other magnetic ferrites such as manganoferrite  $\text{MnFe}_2\text{O}_4$ , cobalt ferrite  $\text{CoFe}_2\text{O}_4$  and nickel ferrite  $\text{NiFe}_2\text{O}_4$ . Normally, the content of magnetic ferrite in the particles will be above 5%.

According to the invention there are particularly used compact or porous particles which contain groups which may have the effect that the iron salt is drawn into the particles and is possibly bound therein. These groups may be incorporated in the particles by preparing the polymer from a monomer containing these groups. Examples of monomers which have been found to be particularly suitable, are dimethylamino-ethylmethacrylate, N-(dimethylaminopropyl)-methacrylic amide and vinyl pyridine which will bind the iron salts with coordinate bonding. Other examples of suitable monomers are such which

contain ethylene oxide groups ( $-\text{CH}_2-\text{CH}_2-\text{O}-$ ) or alkylene imine groups ( $-\text{CH}_2-\text{CHR}'-\text{NH}-$ , in which  $\text{R}'=\text{H}$  or alkyl).

It is also possible to bind the iron by means of ionic bonds. By having acid groups on and inside the particles, the iron may be transported from the outer phase of dissolved iron salt to be bound to these groups. Examples of monomers which will provide such acid groups are methacrylic acid, p-vinyl benzoic acid and maleic anhydride. The iron salt-binding groups may also be attached to the premade polymers. Thus, it is possible to prepare a copolymer from a monomer mixture which essentially consists of vinyl monomer with epoxy group(s) such as glycidyl methacrylate:



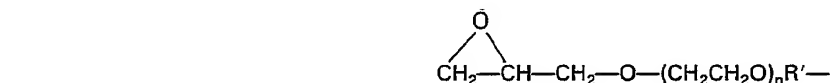
By treating the final polymer with substances which react with epoxy groups and which contain N-groups, said groups will become covalently bonded on and inside the particles. It is for instance possible to treat polymer particles containing epoxy groups with ethylene diamine to form  $-\text{CH}_2-\text{NH}-\text{CH}_2-\text{CH}_2-\text{NH}_2$  groups, or with ethylene oxide group-containing substances such as  $\text{NH}_2-\text{R}-(\text{CH}_2\text{CH}_2\text{O})_n\text{R}'$  or  $\text{HOOCRCOO}(\text{CH}_2\text{CH}_2\text{O})_n\text{R}'$ , wherein R is a suitable aliphatic or aromatic group,  $\text{R}'$  is hydrogen or alkyl, and n is an integer from 1 to 500, to introduce  $-(\text{CH}_2-\text{CH}_2-\text{O})_n\text{R}'$  groups. For the introduction of  $-(\text{CH}_2-\text{CHR}'-\text{NH})_n\text{H}$  groups it is for instance possible to react polymer particles containing  $-\text{COOH}$  groups with alkylene imine compounds, to form  $-\text{CO}-\text{O}-(\text{CH}_2-\text{CHR}'-\text{NH})_n\text{H}$  groups. For the introduction of amino and/or imino groups in the case the polymer contains ester groups such as  $-\text{COOR}'$  in which  $\text{R}'$  is an alkyl group, it is possible to carry out an aminolysis with an organic amine which contains more than one amino group. Thus, by aminolysis of a polymer containing  $-\text{COOR}'$  groups with diethylene triamine,  $-\text{CONH}-\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$  is formed. These reactions may also have the effect that the particles become more hydrophilic and will swell with  $\text{H}_2\text{O}$  so that iron salts are bound inside the particles.

Another method for the introduction of iron-binding groups comprises the introduction of  $-\text{NH}_2$  groups or  $-\text{CH}_2-\text{NH}_2$  groups on the benzene nucleus in polymer particles prepared by polymerization of a monomer which to a considerable extent contains benzene rings such as styrene and divinylbenzene. Further, after the introduction of  $-\text{CH}_2\text{NH}_2$  onto the benzene nucleus, it is possible to introduce  $(\text{CH}_2\text{CH}_2\text{O})_n\text{R}'$  groups by reaction with



in which  $\text{R}'$  and n are as above. It is also possible to introduce  $\text{CH}_2\text{Cl}$  groups on the benzene nucleus and react these groups with  $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_n\text{R}'$  or  $\text{NH}_2(\text{CH}_2\text{CH}_2\text{NH})_n\text{NH}_2$ .

The ethylene oxide chain may also be introduced into the final polymer by reacting such a polymer which contains acid groups, with the epoxide



On polymers which contain benzene nuclei, it is possible to introduce  $-\text{NH}-\text{NH}_2$  groups onto the benzene nucleus. If particles made from acrylates are treated with hydrazine,  $-\text{CONH}-\text{NH}_2$  groups are formed.

Similarly, acid groups may be introduced into the final polymer particles. This may for instance be obtained by hydrolysing a polymer which contains ester groups. Similarly, by known methods it is possible to introduce sulphonic acid groups and carboxylic acid groups into the polymer which has been prepared from styrene and/or styrene-derivatives and admixture of these with divinyl benzene.

By a) preparation of a polymer from a monomer containing N-groups, hydroxy, ethylene oxide or acid groups, by b) posttreatment of an epoxide group-containing polymer with substances such as ethylene diamine, by c) posttreatment of a polymer containing carboxylic acid groups with alkylene imine, by d) posttreatment of a polymer which contains ester groups, with an organic amine having more than one  $-\text{NH}_2$  or  $-\text{NH}$  group, and similarly by e) posttreatment of acrylate particles with hydrazine, it is possible to obtain particles which swell in water or a mixture of water and organic solvents, which will promote the introduction of iron salt into the particles and have the effect that more iron salt is bound. The polymer particles may also be prepared as porous particles having a macroporous structure, i.e. a firm pore structure. In this case the iron salts may be bound in a single layer to the surface inside the pores, but since this surface is very large, a relatively high content of iron inside the particles will nevertheless be obtained. In other cases the iron compound may to a greater or smaller extent fill the pores. Porous particles having a macroporous structure may be prepared by groups which bind iron salts directly, or the particles may be posttreated for the introduction of said groups as described above.

In the case of porous particles having a large surface, it is also possible to introduce iron salt into the particles by coating the interior surface with substances which contain iron-binding groups and which are bound strongly to the surface, before the addition of iron salts, or said substance is added together with the iron salt. Such substances are for instance polyamine amide with limited chain length or substances which contain one or preferably more acid groups or acid groups combined with other groups which provide a strong bonding of iron salts. With porous particles it is possible to use iron salts in which the anionic group is so large and is so hydrophobic that it is bound directly to the interior surface by physical adsorption.

After the particles and the iron salts have been mixed, the pH is raised and iron hydroxide is formed. If one has groups which bind iron salts and these are primary, secondary or tertiary amines, polyethylene oxide groups or anions of acids, one will preferably add a mixture of a divalent and trivalent salt in a ratio which will result in an amount of  $\text{Fe(OH)}_2$  and  $\text{Fe(OH)}_3$  after precipitation which is such that the mixture may result in  $\text{Fe}_3\text{O}_4$ . It is then a particular and important feature that the particles contain groups which attract the iron salt from the outer phase and bind it on and inside the particles so that by raising the pH there will not be an essential precipitation of  $\text{Fe(OH)}_3$  in the outer phase outside the particles.

If the particles which are swollen by the liquid in the outer phase or the porous particles filled with the liquid from the outer phase do not contain groups which bind iron salts, only some of the iron salt will be found inside the particles, and by raising the pH an essential part of the added trivalent iron salt will then be precipitated in the outer phase, which would have the effect that less magnetic iron oxide would be formed inside the particles and also that an essential amount of magnetic iron oxide would be present in the outer phase with subsequent complicated purification processes.

In the case of particles prepared with some polyvinyl monomer (i.e. a monomer containing several vinyl groups, such as divinyl benzene), it is possible to swell the particles in organic solvents, and iron salts which are soluble in these solvents may then be introduced. Also in this case it is advantageous that the particles contain groups which will bind the iron salts so that upon the subsequent transfer of the particles to water the iron salts will remain bound inside the particles. If iron salts containing hydrophobic anions are used, such as iron laurate, the iron compounds will remain in the particles when these are transferred to water, and specific iron-binding groups are not of the same importance. This will also be the case when solid, porous particles having hydrophobic structure are used.

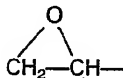
In a particular embodiment of the present invention porous particles containing  $\text{NO}_2$  groups bound to the benzene nuclei are prepared. These particles may for instance be prepared by the preparation of porous particles from nitrostyrene and divinyl benzene in an ordinary manner, i.e. in the presence of inert solvents which are removed after the polymerization, or porous particles may be prepared from styrene or styrene derivatives and divinyl benzene, and then nitro groups are introduced onto the benzene groups according to ordinary methods.

In these cases where nitro groups are present in porous particles, only divalent iron salt is used. The nitro groups will only to a small extent have the effect that the iron salt is transported from the outer phase into the particles. However, when the pH is raised and  $\text{Fe(OH)}_2$  is formed, an oxidation will take place inside the particles by means of  $-\text{NO}_2$  groups which will oxidize  $\text{Fe(OH)}_2$  to  $\text{Fe(OH)}_3$  in such an amount that the ratio between di- and trivalent iron corresponds to that of  $\text{Fe}_3\text{O}_4$ . Thereby constantly more  $\text{Fe(OH)}_2$  is transferred from the outer phase to the pores of the particles. This process is accelerated by the fact that the oxidation of  $\text{Fe(OH)}_2$  by  $-\text{NO}_2$  groups has the effect that the  $-\text{NO}_2$  groups are converted to groups in which the nitrogen has a higher electron density and thereby acquires an increased ability to bind iron salt.

The same principle, i.e. oxidation of added divalent iron salt with an oxidizing nitro component, may also be carried out when the oxidizing nitro component is  $-\text{ONO}_2$  groups or  $\text{ONO}$  groups.

These groups may for instance advantageously be attached to porous particles which contain a large number of hydroxy groups on the surface by allowing these to react with  $\text{NHO}_3$  or  $\text{HNO}_2$ .

Examples of such polymers are macroreticular porous particles prepared with a substantial part of hydroxyethylmethacrylate in the monomer mixture. Other examples are porous particles having an essential content of glycidyl methacrylate in the monomer mixture. In this case the epoxy groups



may be reacted directly with  $\text{HNO}_3$  or  $\text{HNO}_2$ , or hydroxy groups may be introduced by reacting epoxy groups with for instance aminoethanol.

In the methods involving the formation of  $\text{Fe(OH)}_2$  and  $\text{Fe(OH)}_3$  on and in the particles it is often found that already by the formation of this mixture, the particles have become magnetic directly. A more complete magnetization with formation of  $\text{Fe}_3\text{O}_4$  is obtained by heating. Usually it is sufficient to heat the particles in aqueous dispersion to a temperature below  $100^\circ\text{C}$ . The particles may be isolated by centrifugation or filtration or may be extracted with a magnet and dried, and may possibly also be heated in dry condition.

If either di- or trivalent iron hydroxide in or on the particles has been formed in any of the above processes, it is also possible to convert the hydroxide to the desired mixture of di- and trivalent iron hydroxide. Divalent iron hydroxide may for instance be oxidized by the addition of a suitable oxidizing

agent, such as nitrate ion or an organic nitro compound, or the oxidation may for instance be carried out by blowing oxygen through.

In magnetite,  $\text{Fe}_3\text{O}_4$ , the ratio between di- and trivalent iron is 1:2. It is therefore suitable to use a mixture of iron salts with approximately this ratio between di- and trivalent salts when no normally  
 5 reducing/oxidizing groups are present. If the ratio  $\text{Fe}^{++}/\text{Fe}^{+++}$  after the raise of the pH is essentially above 1:2, the formed hydroxides are oxidized.

In the process described above in which a mixture of 2- and 3-valent iron salt or a 2-valent iron salt which is oxidized, is used, ferroferrites  $\text{FeFe}_2\text{O}_4$  ( $=\text{Fe}_3\text{O}_4$ ) are formed. In these cases it is also possible to use a mixture of iron salts with other metal salts which will provide other types of magnetic ferrites. Thus,  
 10 according to the same principles it is also possible to form manganoferrite,  $\text{MnFe}_2\text{O}_4$  cobalt ferrite,  $\text{CoFe}_2\text{O}_4$  or nickel ferrite  $\text{NiFe}_2\text{O}_4$ .

If a mixture of a water-soluble salt of a 2-valent metal, such as  $\text{MnX}_n$ ,  $\text{CoX}_n$  or  $\text{NiX}_n$ , in which X is a 2/n-valent anion ( $n=2, 1, 2/3$  or  $1/2$ , particularly 1 or 2) and a water-soluble salt of 3-valent iron is used, the salt mixtures are precipitated as hydroxides inside the particles and are then heated to a suitable  
 15 temperature to form the corresponding magnetic metal ferrites. If a salt of 2-valent iron is used in admixture with the other metal salt, the divalent iron in the form as iron hydroxide inside the particles is oxidized to trivalent iron under conditions which provide the desired metal ferrite. The oxidation may take place by means of oxidizing groups such as  $-\text{NO}_2$ ,  $-\text{ONO}$  or  $-\text{ONO}_2$  which has been introduced onto the polymers, or it may take place by the addition of suitable oxidizing agents. In this case it is possible to  
 20 obtain a mixture of ferroferrite with other ferrites,  $\text{MeFe}_2\text{O}_4$ , in which Me represents Co, Ni or Mn. An advantage by using a mixture of iron salt with other metal salts is that in this case there is no risk of overoxidation of the iron, since in that case there will only be formed  $\text{MeFe}_2\text{O}_4$  at the expense of  $\text{FeFe}_2\text{O}_4$ .

The polymer particles used as starting material for the preparation of magnetic particles may in the principle be prepared according to all the methods which are known for the preparation of dispersions of  
 25 polymeric particles. This includes a preparation by ordinary emulsion polymerization, in which the monomer is added to water with or without emulsifier, polymerization is carried out by means of a water-soluble initiator, and the particles are initiated in the aqueous phase. The method will result in particles in the range up to about  $0.6 \mu\text{m}$  in diameter. The size and the monodispersity increase with decreasing amount of emulsifier. The particles may also be prepared by initiation in drops, which may be  
 30 obtained in different ways. It is for instance possible to homogenize a mixture of monomer with a small amount of a water-insoluble material having a water-solubility less than  $10^{-3} \text{ g/l H}_2\text{O}$  with water and emulsifier, which will provide stable monomer emulsions, and then polymerize with addition of initiator and heating. The water-insoluble substance used may be a water-insoluble monomer. If desired, it is possible to use an oil-soluble initiator which is added together with the monomer before the homogenization. Possibly this initiator may in itself serve as the water-insoluble substance which provides  
 35 stable monomer emulsions. By this method initiation may take place exclusively inside the drops.

It is also possible to homogenize in a first step a water-insoluble substance having a water-solubility less than  $10^{-3} \text{ g/l H}_2\text{O}$  with water and emulsifier. Then monomer is added which will diffuse into the drops of water-insoluble substance and polymerize by means of water-soluble initiator or oil-soluble initiator  
 40 added together with or after the monomer and which has such a high water-solubility that it just like the monomers may diffuse through the water and into the drops of the water-insoluble substance. Also in this case the water-insoluble substance used during the homogenization may be an initiator.

The polymer particles may also be prepared by seed processes. In this case a seed of polymer particles dispersed in water is used, possibly a mixture of water and an organic solvent which is soluble in water, and the desired monomers are introduced into the polymer particles before polymerization either with a  
 45 water-soluble initiator or with an oil-soluble initiator added together with or after the monomers. In many cases, particularly for the preparation of larger particles, it is possible to use a seed technique which comprises the preparation in a first step of particles which in addition to the polymer molecules also contain a water-insoluble substance having a relatively low molecular weight. Such a method has been  
 50 described in Norwegian patent No. 142.082. When the water-insoluble substance having a water-solubility of less than  $10^{-3} \text{ g/l H}_2\text{O}$  and having a relatively low molecular weight is present in the particles, these are as described in said patent capable of absorbing much more monomer than ordinary polymer particles.

A specific embodiment of this method which has also been found to be favourable for the preparation of polymer particles which are later converted to magnetic particles, comprises that the water-insoluble  
 55 substance used for swelling the polymer particles in the first step, is an oil-soluble initiator which is used for polymerization after the monomer has diffused into the particles.

The preparation of polymer particles by seed technique is particularly favourable when it is desired to prepare spherical magnetic particles which are monodisperse and which will therefore also contain the same amount of magnetic ferrite in each particle. In this case one starts with a monodisperse seed, i.e. a  
 60 polymer dispersion where all the particles have approximately the same size, for instance a standard deviation of less than 5%. The standard deviation for the content of magnetic ferrite will then normally be less than 10%. The polymeric particles may also be prepared by ordinary suspension polymerization. In this case large particles are obtained directly, but with a broad size-distribution.

The particles prepared according to the above methods by polymerization in drops or swelled  
 65 particles, may be obtained as porous particles by using ordinary methods which involve the use of a

mixture of monomers at least one of which is a polyvinyl compound, and in addition inert solvents for the monomers are present, which are removed after the polymerization. For the preparation of the polymer particles it is possible to use ordinary vinyl monomers and polyvinyl monomers and mixtures thereof. Examples of vinyl monomers which are used, are styrene and styrene derivatives, maleic anhydride, acrylates and methacrylates such as methylacrylate, methylmethacrylate, ethylacrylate, ethylmethacrylate, butylacrylate and butylmethacrylate, and vinyl esters such as vinyl acetate. Examples of polyvinyl monomers which may be used, comprise divinyl benzene, ethylene glycol dimethacrylate, trimethylolpropane trimethacrylate and adipic acid divinyl ester. As emulsifier ordinary ionic or non-ionic emulsifiers may be used. As initiator water-soluble initiators such as potassium persulphate and  $\text{H}_2\text{O}_2$  or oil-soluble initiators such as azobisisobutyric nitrile and benzoyl peroxide may be used. As inert materials which are used to stabilize emulsions of monomer or to increase the swelling capacity of the polymer particles, one may use substances which are disclosed in Norwegian patents 139.410 and 142.082. Examples are alkanes having a chain length above 10 C-atoms, halogenated alkanes, esters and diesters such as dioctyl adipate. Examples of water-insoluble initiators used as additive for increasing the swelling of particles with monomer as well as for polymerization, are dioctanoyl peroxide and didecanoyl peroxide.

The preparation of dispersions of polymers in water may also be carried out by dissolving the polymer in a solvent which is slightly soluble in water and then mixing the solution of the polymer with water and emulsifier and subjecting the mixture to strong shear forces, for instance by means of ultraturrax stirrer or pressure homogenizer, to obtain a fine emulsion of the polymer solution in water with varying drop size. By removing the solvent, for instance by evaporation, there will be formed a finely divided dispersion of polymer particles in water.

The incorporation of metal salts in the particles may take place before or after the removal of the organic solvent. In this case where the polymer dispersion is prepared from a final polymer it is irrelevant how the polymer has been prepared. It may have been prepared by radical polymerization of vinyl monomers as described above, but it may also have been prepared by any process which results in polymers, such as cationic and anionic polymerization, stepwise addition polymerization and condensation polymerization.

#### Example 1

100 ml of methylmethacrylate, 90 ml of glycidyl methacrylate, 10 ml of ethyleneglycol dimethacrylate and 1750 ml of  $\text{H}_2\text{O}$  were mixed in a reactor. The mixture was then subjected to rapid stirring for 30 min. Then, 2.0 g of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  dissolved in 50 ml of water were added. The temperature was raised to  $65^\circ\text{C}$ , and polymerization was carried out for 6 hours. After polymerization a latex containing 10% of polymer, particle size 0.2—0.3  $\mu\text{m}$ , was obtained.

100 ml of the latex were treated with 100 ml of ethylene diamine at  $80^\circ\text{C}$  for 3 hours. After the reaction excess of ethylene diamine was removed by dialysis for 10 days, with change of water every day.

Elementary analysis showed that the particles contained 4.6 percent by weight of N. 50 ml of dialyzed latex containing 5 g of particles treated with ethylene diamine were cooled down to  $10^\circ\text{C}$ .

811 mg (3.0 mmole)  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were dissolved in 20 ml of water and cooled down to  $10^\circ\text{C}$ . Similarly, 338 mg (1.7 mmole)  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were dissolved in 20 ml of water and cooled down to  $10^\circ\text{C}$ . The two iron chloride solutions were combined and then mixed with the latex in a rotating container which was rapidly evacuated down to 10 mm Hg. After 20 minutes 10 ml cold ( $10^\circ\text{C}$ ) ammonia solution (25%) were added by suction. The vacuum was then eliminated, and the temperature was raised to  $80^\circ\text{C}$ . After 30 minutes at  $80^\circ\text{C}$ , the mixture was cooled and the particles separated from the solution by centrifugation. The particles were washed several times with water to remove excess of ammonia and ammonium chloride formed. After this treatment the particles contain magnetic iron oxide. The iron content in the particles was found to be 4.9%.

#### Example 2

200 ml of methylmethacrylate, 10 ml of stearyl methacrylate, 75 ml of glycidylmethacrylate, 15 g of ethylene glycol dimethacrylate, 1500 ml of  $\text{H}_2\text{O}$  and 4.5 cetyltrimethylammonium bromide were homogenized to an emulsion with a drop size of 0.2—0.4  $\mu\text{m}$ . The mixture was transferred to a 1 l reactor. 1.9 g of  $\text{NaHCO}_3$  and 1150 ml of  $\text{H}_2\text{O}$  were added. The reactor was evacuated and filled with 99.9%  $\text{N}_2$  in several operations, and then 9 g of  $\text{H}_2\text{O}_2$  (30% active) dissolved in 50 ml of  $\text{H}_2\text{O}$  were added. The temperature was raised to  $60^\circ\text{C}$ . After the polymerization a latex having a particle size of 0.2—0.4  $\mu\text{m}$  and a solids content of 9.5% was obtained.

Treatment with ethylene diamine for the introduction of primary amino groups was carried out as described in example 1. After this treatment the particles contained 2.8% N.

To 30 ml of dialyzed latex containing 3 g of particles treated with ethylene diamine were added iron chloride and ammonia solution as described in example 1. In this case 514 mg (1.9 mmole) of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 20 ml of water, 219 mg (1.1 mmole) of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  in 20 ml of water and 8 ml of ammonia solution (25%) were added. The further treatment and recovery of the particles were carried out as described in example 1.

The final particles contain magnetic iron oxide. The iron content in the particles was found to be 5.2%.

## Example 3

10 ml of hexadecane, 50 ml of H<sub>2</sub>O and 0.15 g of Na-lauryl sulphate were homogenized to an emulsion with a drop size of 0.2—0.7 µm. The mixture was transferred to a reactor. 800 ml of H<sub>2</sub>O and 1.0 g of Na-lauryl sulphate were added. A mixture of 130 ml of methylmethacrylate, 60 ml of glycidylmethacrylate, 5 10 ml of ethylene glycoldimethacrylate and 4 g of azo-bis-isobutyronitrile was added slowly under stirring. After 2 hours the temperature was raised to 60°C. The polymerization takes place for 6 hours, and a latex having a particle size of 0.5—2 µm and a solids content of 19% is obtained. Treatment with ethylenediamine for the introduction of primary amino groups was carried out as described in example 1. After the reaction, the particles were separated and washed several times with water in a centrifuge to 10 remove excess of ethylene diamine.

Elementary analysis showed that the particles contained 3.5% N.

To 25 ml of a latex containing 2.9 g of particles treated with ethylene diamine there were added iron chloride and an ammonia solution as described in example 1. In this case 649 mg (2.4 mmole) of FeCl<sub>3</sub> · 6H<sub>2</sub>O dissolved in 20 ml of water, 278 mg (1.4 mmole) of FeCl<sub>2</sub> · 4H<sub>2</sub>O dissolved in 20 ml of water and 15 10 ml of an ammonia solution (25%) were added. The further treatment and the recovery of the particles were carried out as described in example 1.

The final particles contain magnetic iron oxide. The iron content in the particles was found to be 6.6%.

## Example 4

20 10 ml of dioctanoylperoxide, 30 ml of H<sub>2</sub>O and 0.03 g of Na-laurylsulphate were homogenized to an emulsion having a drop size of 0.2—0.7 µm.

The mixture was transferred to a reactor. 800 ml of water and 1.0 g of Na-laurylsulphate were added. Under stirring at 25°C a mixture of 110 ml of methylmethacrylate, 90 ml of glycidylmethacrylate and 10 ml of ethylene glycoldimethacrylate was added slowly. After 2 hours the temperature was raised to 65°C. 25 When the polymerization was terminated, a latex having a particle size of 0.5—2 µm and a solids content of 19% was obtained. The treatment with ethylene diamine for the introduction of primary amino groups was carried out as described in example 3. Elementary analysis showed that the particles contained 4.6% N.

To 30 ml of a latex containing 2 g of particles treated with ethylene diamine there were added iron chloride and an ammonia solution as described in example 1. In this case 514 mg (1.9 mmol) of FeCl<sub>3</sub> · 6H<sub>2</sub>O 30 in 20 ml of water, 219 mg (1.1 mmole) of FeCl<sub>2</sub> · 4H<sub>2</sub>O in 20 ml of water and 10 ml of an ammonia solution (25%) were added. The further treatment and the recovery of the particles were carried out as described in example 1.

The final particles contain magnetic iron oxide. The iron content in the particles was found to be 7.5%.

## 35 Example 5

10 ml of dioctanoyl peroxide, 30 ml of H<sub>2</sub>O and 0.03 g of Na-laurylsulphate were homogenized to an emulsion with a drop size of 0.2—0.7 µm. The mixture was transferred to a reactor. 800 ml of water and 1.0 g of Na-laurylsulphate were then added. Under stirring at 25°C a mixture of 40 ml of glycidylmethacrylate, 40 ml of ethylene glycoldimethacrylate and 120 ml of cyclohexanol was slowly added. After 2 hours the 40 temperature was raised to 60°C. After the polymerization was ended, a latex having a particle size of 0.5—2.0 µm was obtained. The cyclohexanol was removed by washing several times with water and isopropanol. After drying a porous powder having a specific surface of 115 m<sup>2</sup>/g (BET-method) was obtained.

10 g of the porous particles were treated with 100 ml of ethylenediamine at 80°C for 3 hours. Unreacted 45 ethylene diamine was removed by centrifugation and several washings with H<sub>2</sub>O. Elementary analysis showed that the particles contained 5.8% N. 3 g of dry particles treated with ethylenediamine were added to 20 ml water and iron chloride and ammonia solution were added thereto as described in example 1. In this case 1954 mg (3.9 mmole) of FeCl<sub>3</sub> · 6H<sub>2</sub>O in 20 ml of water, 457 mg (2.3 mmole) of FeCl<sub>2</sub> · 4H<sub>2</sub>O in 20 ml of water and 15 ml of ammonia solution (25%) were added. The further treatment and the recovery of the 50 particles were carried out as described in example 1.

The final particles contain magnetic iron oxide. The iron content in the particles was found to be 10.0%.

## Example 6

5 ml of dioctanoyl peroxide, 50 ml of water and 0.15 g of Na-laurylsulphate were homogenized to an 55 emulsion with drops size 0.15—0.25 µm. This emulsion was mixed with a latex consisting of polystyrene particles having a diameter of 0.5—1.0 µm. The amount of latex that was added (40 ml) contained 5 ml of polystyrene particles and 35 ml of H<sub>2</sub>O. After careful stirring for 24 hours, the mixture was transferred to a reactor containing 800 ml of water and 2.4 g of Na-laurylsulphate. 164 ml of methylmethacrylate, 140 ml of glycidylmethacrylate and 16 ml of ethylene glycoldimethacrylate were slowly added. After stirring for 2 60 hours 800 ml of H<sub>2</sub>O were added, and the temperature was raised to 60°C. After the polymerization a latex having a particle size of 2.4 µm and a solids content of 14.5% was obtained.

The treatment with ethylenediamine for introduction of the primary amino groups was carried out as described in example 1. Removal of unreacted ethylene diamine was carried out as in example 3.

Elementary analysis showed that the particles contained 4.5% N.

65 2.5 g dry particles treated with ethylene diamine were transferred to 20 ml of water. The particles were



treated with iron chloride and ammonia solution as described in example 1. In this case 608 mg (2.3 mmole) of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 20 ml of water, 249 mg (1.3 mmole) of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  in 20 ml of water and 10 ml of ammonia solution (25%) were added.

The particles were recovered by filtration and washing with water and finally with methanol before drying.

After the treatment the particles contained magnetic iron oxide. The iron content was found to be 7.1%.

#### Example 7

5 ml of dioctanoyl peroxide, 50 ml of water and 0.15 g of Na-laurylsulphate were homogenized to an emulsion with a drop size of 0.15–0.25  $\mu\text{m}$ . This emulsion was mixed with a latex consisting of monodisperse polystyrene particles having a diameter of 0.53  $\mu\text{m}$  (determined by electron microscopy). The amount of latex added (31.25 ml) contained 5 ml of polystyrene particles and 26.25 ml of  $\text{H}_2\text{O}$ . After careful stirring for 24 hours, the mixture was transferred to a reactor containing 800 ml of water and 2.5 g of Na-laurylsulphate. 304 ml of glycidylmethacrylate and 16 ml of ethylene glycoldimethacrylate were slowly added. After stirring for 2 hours 800 ml of  $\text{H}_2\text{O}$  were added, and the temperature was raised to 60°C. After the polymerization a monodisperse latex having a particle size of 2.0  $\mu\text{m}$  (determined by electron microscopy) and a solids content of 14.6% was obtained.

Treatment with ethylene diamine for introduction of primary amino groups was carried out as described in example 1. Removal of unreacted ethylene diamine was carried out as described in example 3. Elementary analysis showed that the particles contained 9.5% N.

2 g of dry particles treated with ethylene diamine were transferred to 20 ml of water. The particles were treated with iron chloride and ammonia solution as described in example 1. In this case 930 mg (3.4 mmole) of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 20 ml of water, 390 mg (2.0 mmole)  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  in 20 ml of water and 15 ml of ammonia solution (25%) were added. The recovery of the particles was carried out as described in example 6. After the treatment the particles contain magnetic iron oxide. The iron content was found to be 12.5%.

#### Example 8

5 ml of dioctyl adipate, 42.5 ml of water, 7.4 ml of acetone and 0.15 g of Na-laurylsulphate were homogenized to an emulsion with a drop size of 0.2–0.3  $\mu\text{m}$ . This emulsion was mixed with a latex consisting of monodisperse polystyrene particles having a diameter of 1.04  $\mu\text{m}$  (determined by electron microscopy). The amount of latex added (25 ml) contained 2.5 ml of polystyrene particles and 22.5 ml of  $\text{H}_2\text{O}$ . After careful stirring for 20 hours the acetone was removed by evaporation *in vacuo*, and the latex was transferred to a reactor containing 818 ml of  $\text{H}_2\text{O}$  and 2.3 g of Na-laurylsulphate. A mixture of 270 ml of glycidyl methacrylate, 14 ml of ethylene glycoldimethacrylate and 5.7 g of benzoyl peroxide was added slowly under vigorous stirring. After stirring for 2 hours 818 ml of  $\text{H}_2\text{O}$  were added, and the temperature was raised to 60°C. After the polymerization a monodisperse latex having a particle size of 5.0  $\mu\text{m}$  (determined by electron microscopy) was obtained. Treatment with ethylene diamine for the introduction of primary amino groups was carried out as described in example 1. Removal of unreacted ethylene diamine was carried out as described in example 3. Elementary analysis showed that the particles contained 7.00% N.

3 g of particles treated with ethylene diamine were transferred to 25 ml of water. The particles were treated with iron chloride and ammonia solution as described in example 1. In this case 716 mg (2.6 mmole) of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 25 ml of water, 301 mg (1.5 mmole) of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  in 25 ml of water and 20 ml of ammonia solution (25%) were added.

The recovery of the particles was carried out as described in example 6. After the treatment the particles contain magnetic iron oxide. The iron content was found to be 7.0%.

#### Example 9

10 ml of dioctanoyl peroxide, 85 ml of water, 15 ml of acetone and 0.30 g of Na-laurylsulphate were homogenized to an emulsion with a drop size of 0.2–0.3  $\mu\text{m}$ . This emulsion was mixed with 37 ml of a latex consisting of monodisperse polymer/oligomer particles (in which each particle contained 70% oligomer styrene with molecular weight 2500 and 30% polystyrene) having a diameter of 1.0  $\mu\text{m}$  (determined by Coulter Nano Sizer). The amount of latex added contained 4 ml of polymer/oligomer particles and 33 ml of  $\text{H}_2\text{O}$ . After careful stirring for 20 hours acetone was removed by evaporation *in vacuo*. The amount of latex after the removal of acetone, was 132 ml.

A mixture of 81.5 ml of glycidyl methacrylate, 122 ml of ethyleneglycol dimethacrylate, 314.5 ml of cyclohexanol, 1450 ml of  $\text{H}_2\text{O}$  and 20 g of polyvinylpyrrolidone (molecular weight 360,000) was emulsified in an ultraturrax mixer for 1 1/2 minute. The emulsion was transferred to a reactor, and the above latex residue of 132 ml was added. This mixture was stirred with a moderate stirring rate for 2 hours. Then 1450 ml of water were added, and the temperature was raised to 60°C. After the polymerization the reactor was cooled down, and cyclohexanol was removed by several times washing with water and isopropanol. After drying 155 g of monodisperse porous particles having a diameter of 4.8  $\mu\text{m}$  (determined by electron microscopy) and a specific surface of 151  $\text{m}^2/\text{g}$  polymer (BET) were obtained.

Treatment with ethylene diamine for the introduction of primary amino groups was carried out as



described in example 5. Unreacted ethylene diamine was removed by centrifugation and several times washing with water. Elementary analysis of dry particles showed that they contained 4.9% N.

5 g of particles treated with ethylene diamine were transferred to 40 ml of water. The particles were treated with iron chloride and ammonia solution as described in example 1. In this case 1.50 g (5.5 mmole) of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 25 ml of water, 0.64 g (3.0 mmole) of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  in 25 ml of water and 25 ml of ammonia solution (25%) were added.

The recovery of the particles was carried out as in example 6. After the treatment the particles contain magnetic iron oxide. The iron content was found to be 8.5%.

#### 10 Example 10

5 ml of dioctanoyl peroxide, 42.5 ml of  $\text{H}_2\text{O}$ , 7.5 ml of acetone and 0.15 g of Na-laurylsulphate were homogenized to an emulsion with a drop size of 0.2–0.4  $\mu\text{m}$ . This emulsion was treated with a latex consisting of monodisperse polymer/oligomer particles having a diameter of 1.0  $\mu\text{m}$ . The amount of latex added, 18.5 ml, contained 2 ml of polymer/oligomer particles and 16.5 ml of  $\text{H}_2\text{O}$ . After careful stirring for 20 hours the acetone was removed by evaporation *in vacuo*, residue 66 ml. This residue was transferred to a reactor containing 800 ml of  $\text{H}_2\text{O}$  and 3.25 g of Na-laurylsulphate. A mixture of 40 ml of dimethylaminoethylmethacrylate, 90 ml of ethylene glycoldimethacrylate and 200 ml of cyclohexanol was added slowly under efficient stirring. After 2 hours 800 ml of water were added, and the temperature was raised to 60°C. After 6 hours of polymerization, the reactor was cooled and cyclohexanol was removed from the particles by several washings with  $\text{H}_2\text{O}$  and isopropanol. After drying there were obtained 110 g of monodisperse porous polymer particles having a diameter of 4.7  $\mu\text{m}$  and a specific surface of 222  $\text{m}^2/\text{g}$  polymer (BET). Elementary analysis showed that the polymer particles contained 1.7% N, i.e. 1.2 mmole of



30 groups per g polymer.

5 g of particles were transferred to 50 ml water and treated with iron chloride and ammonia solution as described in example 1. In this case 1027 mg (3.8 mmole) of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 25 ml of water, 434 mg (2.2 mmole) of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  in 25 ml of water and 20 ml ammonia solution (25%) were added.

After the treatment was brought to an end, the particles were filtered from the solution and washed with water and finally with methanol. The particles were then dried.

After the treatment the particles contain magnetic iron oxide. The iron content was found to be 6.1%.

#### Example 11

2 ml of Trigonox 21 S (t-butyl-peroxy-2-ethylhexanoate), 2 ml of dioctyladipate, 40 ml of water and 0.12 g of Na-laurylsulphate were homogenized to an emulsion with a drop size of 0.15–0.25  $\mu\text{m}$ . This emulsion was mixed with a latex consisting of monodisperse polymer/oligomer particles having a diameter of 1.0  $\mu\text{m}$ . The amount of latex added, 18.5 ml, contained 2 ml of polymer/oligomer particles and 16.5 ml of  $\text{H}_2\text{O}$ . After careful stirring for 24 hours the mixture was transferred to a reactor containing 700 ml of  $\text{H}_2\text{O}$  and 2.5 g of Na-laurylsulphate. A mixture of 33 ml of 4-vinylpyridine, 50 ml of divinylbenzene (50%) and 167 ml of toluene was slowly added. After vigorous stirring for 16 hours 1.5 g of Berol 292 (nonylphenol ethoxylate with 20 moles of ethylene oxide per mole nonylphenol) and 750 ml of water were added. The temperature was raised to 70°C, and polymerization was carried out until the reaction was complete.

After cooling the toluene was removed by several extractions with acetone. After drying 70 g of monodisperse porous polymer particles having a diameter of 4.7  $\mu\text{m}$  and a specific surface of 193  $\text{m}^2/\text{g}$  polymer (BET) were obtained. Elementary analysis showed that the particles contained 6.0% N.

654 mg (2.4 mmole) of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  were dissolved in 25 ml of water and cooled to 10°C. Similarly, 274 mg (1.4 mmole) of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were dissolved in 25 ml of water and cooled to 10°C. These two solutions were combined, and then 50 ml of methanol precooled to 10°C were added. To this mixture 1 g of dry particles were added, and it was all transferred to a rotating container which was evacuated to 10 mm Hg. After 30 minutes 10 ml cold (10°C) ammonia solution (25%) were added by suction. The vacuum was then eliminated, and the temperature was raised to 80°C. After 15 minutes at 80°C the mixture was cooled and the particles filtered off. The particles were washed with water and finally with methanol and were then dried. After the treatment the particles contain magnetic iron oxide. The iron content was found to be 16.4%.

#### Example 12

5 ml of dioctanoyl peroxide, 42.5 ml of water, 7 ml of acetone and 0.15 g of Na-laurylsulphate were homogenized to an emulsion with a drop size of 0.2–0.3  $\mu\text{m}$ . This emulsion was mixed with a latex consisting of monodisperse polystyrene particles having a diameter of 0.53  $\mu\text{m}$ . The amount of latex added (20.83 ml) contained 3.33 ml of polystyrene particles and 17.50 ml of  $\text{H}_2\text{O}$ . After careful stirring for 20 hours

acetone was removed *in vacuo* and the latex transferred to a reactor containing 800 ml of water and 3.25 g of Na-laurylsulphate. A mixture of 100 ml of divinylbenzene (50%) and 200 ml of toluene was slowly added. After vigorous stirring for 16 hours 800 ml of H<sub>2</sub>O and 4.0 g of Berol 292 (nonylphenol ethoxylate with 20 moles of ethylene oxide per mole nonylphenol) were added. The temperature was raised to 70°C and polymerization was carried out until the reaction was complete.

After cooling toluene was removed by several extractions with acetone. After drying 82 g of monodisperse porous particles having a diameter of 2.0 µm and a specific surface of 472 m<sup>2</sup>/g polymer (BET) were obtained.

5 g of dry particles were transferred to a mixture of 50 ml of concentrated nitric acid and 125 ml of concentrated sulphuric acid in 30 minutes under stirring. 40 minutes after the addition of the particles was brought to an end, the reaction mixture was poured into a container containing 1 litre of ice. The particles were filtered from the solution and washed with water (400 ml) and finally with methanol (200 ml). After drying 5 g of the particles were transferred to a rotating container together with 10 g of FeSO<sub>4</sub> · 7H<sub>2</sub>O dissolved in 150 ml of water. The container was then evacuated to 10 mm Hg. After 45 minutes 50 ml of ammonia solution (25%) were added by suction. Then the vacuum was eliminated, and the temperature was raised to 80°C. After 15 minutes at 80°C the mixture was cooled and filtered. First the particles were washed with water (400 ml) and then finally with methanol (200 ml). The particles were then dried. After this treatment the particles contain magnetic iron oxide. The iron content in the particles was found to be 20.0%.

#### Example 13

Monodisperse porous particles were prepared as described in example 12.

5 g of porous particles, 1 g of polyamine amide (Versamid-115) and 100 ml of toluene were mixed and transferred to a rotating container which was then evacuated (10 mm Hg). The temperature in the mixture was kept between 5 and 10°C. After one hour the temperature was raised and the mixture evaporated to dryness.

2 g of these particles in 40 ml of methanol were then treated with iron chloride and ammonia solution as described in example 1 to form ferromagnetic ironoxide in the particles. In this case 520 mg (1.9 mmole) of FeCl<sub>3</sub> · 6H<sub>2</sub>O in 25 ml of water, 220 mg (1.1 mmole) FeCl<sub>2</sub> · 4H<sub>2</sub>O in 25 ml of water and 10 ml of ammonia solution (25%) were added.

The particles were separated from the solution by filtration, washed with water and then finally with methanol. The particles were then dried. The final particles contain magnetic iron oxide. The iron content was found to be 5.2%.

#### Example 14

To a reactor fitted with stirrer of the impeller type 1800 ml of water, 4.8 g of Gelvatol 20—60 (polyvinyl alcohol 80% hydrolyzed) and 0.012 g of Na-laurylsulphate were added. To this a mixture consisting of 80 ml of styrene, 120 ml of divinylbenzene (50%), 200 ml of heptane, 200 ml of toluene and 3 g of azobisisobutyronitrile was added. This was vigorously stirred for 30 minutes before the temperature was raised to 70°C. The polymerization took place under vigorous stirring for 5 hours. After cooling the polymer was filtered from the aqueous phase, and toluene/heptane was removed by extraction several times with acetone. After drying there were obtained 180 g of a porous powder having a particle size of 5—50 µm and a specific surface of 234 m<sup>2</sup>/g.

For the introduction of NO<sub>2</sub> groups and the subsequent treatment with 2- and 3-valent iron to magnetize the particles, the same method as described in example 12 was used.

After the treatment the particles contained magnetic iron oxide. The iron content was found to be 17.3%.

#### Example 15

To a reactor fitted with a blade stirrer 225 ml of water and 0.6 g of Gelvatol 20—60 (polyvinylalcohol 80% hydrolyzed) were added. A mixture consisting of 10 ml of 3-nitrostyrene, 15 ml of divinylbenzene (75%), 25 ml of toluene, 25 ml of heptane and 0.375 g of azobisisobutyronitrile was added thereto. This was subjected to vigorous stirring for 30 minutes before the temperature was raised to 70°C. The polymerization was carried out under vigorous stirring until the reaction was complete. After cooling the polymer was filtered from the aqueous phase and toluene was removed by extraction several times with acetone. After drying there were obtained 23 g of a porous powder having a particle size of 10—60 µm and a specific surface of 254 m<sup>2</sup>/g (BET).

1 g of these porous particles was transferred to a rotating container together with 1.4 g of FeSO<sub>4</sub> · 7H<sub>2</sub>O dissolved in 40 ml of water. The container was then evacuated to 10 mm Hg. After 45 minutes 10 ml of ammonia solution (25%) were added by suction. The vacuum was then eliminated, and the temperature was raised to 80°C. After 15 minutes at 80°C the mixture was cooled and filtered. First the particles were washed with water (100 ml) and finally with methanol (25 ml). The particles were then dried. After this treatment the particles contain magnetic iron oxide. The iron content in the particles was found to be 19.8%.

## Example 16

5.0 ml of dioctanoyl peroxide, 42.5 ml of H<sub>2</sub>O, 7.5 ml of acetone and 0.15 g of Na-laurylsulphate were homogenized to an emulsion with a drop size of 0.2—0.4 μm. This emulsion was treated with 15.72 ml of a latex consisting of monodisperse polystyrene particles having a diameter of 0.46 μm (determined by electron microscopy). The amount of latex added contained 2.5 ml of polystyrene particles and 13.22 ml of H<sub>2</sub>O. After careful stirring for 20 hours the acetone was evaporated *in vacuo*, and the latex was transferred to a reactor containing 800 ml of H<sub>2</sub>O and 3.0 g of Na-laurylsulphate. A mixture of 201.6 ml of methylmethacrylate, 22.4 ml of ethylene glycoldimethacrylate and 96.0 ml methacrylic acid was added slowly with good stirring. After stirring for 1 hour 800 ml of H<sub>2</sub>O were added, and the temperature was raised to 65°C. After polymerization for 2 hours 1.6 g of Berol 292 were added. The polymerization was continued until the reaction was complete, and a monodisperse latex having a particle size of 2.3 μm (determined by electron microscopy) was obtained.

For further treatment the particles were separated from the aqueous phase by centrifugation. The particles were washed with acetone and dried. 2 g of the dry particles were then transferred to 50 ml of a sodium hydroxide solution (2%) in a glass flask fitted with a stirrer. After stirring for 20 minutes the particles were separated from the solution by centrifugation. Alternate washing with water and centrifugation were then carried out until the washings had an approximately neutral pH. The particles were then transferred to 50 ml of water and treated with iron chloride and ammonia solution as described in example 1. In this case 334 mg (1.3 mmole) of FeCl<sub>3</sub> · 6H<sub>2</sub>O in 20 ml of water, 145 mg (0.7 mmole) of FeCl<sub>2</sub> · 4H<sub>2</sub>O in 20 ml of water and 10 ml of ammonia solution (25%) were added. The recovery of the particles was carried out as in example 6. After the treatment the particles contain magnetic iron oxide. The iron content was found to be 5.2%.

## Example 17

Porous, monodisperse particles having a diameter of 2.0 μm prepared as described in example 12 were treated with chloromethyl ether, ClCH<sub>2</sub>OCH<sub>3</sub>, in a known manner for the introduction of —CH<sub>2</sub>Cl on the benzene nucleus. By this treatment porous particles with 1.2 mmole —CH<sub>2</sub>Cl groups per g particles were obtained.

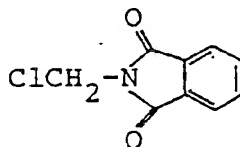
100 ml of polyethylene glycol, HO(CH<sub>2</sub>CH<sub>2</sub>O)<sub>n</sub>H, with mean n=30, 100 ml of tetrahydrofurane and 1.5 g of NaH were mixed in a three-necked flask under an atmosphere of nitrogen and were kept stirring at 50° for 2 hours. 10 g of the chloromethylated particles prepared above were added, and it was heated with reflux for 2 days. After the reaction was brought to an end, the particles were separated off by filtration and they were washed several times with tetrahydrofurane. Finally, the particles were dried *in vacuo*.

2.8 g of the dry particles were treated with iron chloride and ammonia as described in example 1. In this case 1300 mg (4.8 mmole) FeCl<sub>3</sub> · 6H<sub>2</sub>O and 450 mg (2.4 mmole) FeCl<sub>2</sub> · 4H<sub>2</sub>O were used.

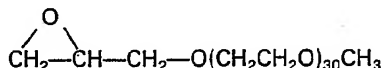
The particles were separated from the solution by filtration and were washed with water and finally with methanol. The particles were then dried. After the treatment the particles contain magnetic iron oxide. The iron content was found to be 10.5%.

## Example 18

Porous, monodisperse particles having a diameter of 2.0 μm prepared as described in example 12, were treated according to known methods, with chloromethylphthalimide,



and then with hydrazine for introduction of —CH<sub>2</sub>NH<sub>2</sub> groups on the benzene nucleus. A product containing 1.3 mmole —CH<sub>2</sub>NH<sub>2</sub> groups per g of the particles was prepared. 5 g of dry particles were treated with 20 g of epoxypolyethylene glycolmonomethylether,



and the mixture was kept under an atmosphere of nitrogen with careful stirring in a three-necked flask at 90° for 24 hours. The particles were then separated by filtration, and washed several times with tetrahydrofurane until all extractable material was removed, and were then dried.

2.8 g of the dry particles were treated with iron chloride and ammonia as described in example 1. In this case 1300 mg FeCl<sub>3</sub> · 6H<sub>2</sub>O and 450 mg of FeCl<sub>2</sub> · 4H<sub>2</sub>O were used.

The particles were separated from the solution by filtration, washed with water and finally with methanol. The particles were then dried. After the treatment the particles contain ferromagnetic ironoxide.

The iron content was found to be 10%.

## Example 19

To 100 ml of an acetone solution containing 6.2 mmoles of  $\text{FeCl}_3$  and 3.1 mmoles of  $\text{FeCl}_2$  there were added 3 g of dry, porous monodisperse particles having polyethylene oxide groups bonded to the benzene nucleus. The preparation of the particles is described in example 18.

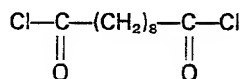
5 The suspension of the particles in acetone was stirred for 30 minutes under an atmosphere of nitrogen. The particles were then filtered off on a suction funnel while all the time a blanket of nitrogen was kept covering the filter cake. When all excess liquid was removed, the particles were treated with a flow of moist  $\text{NH}_3$  vapour. The particles were then washed with water and finally with methanol. The particles then were dried. After the treatment the particles contain magnetic iron oxide. The iron content was found to be 9.5%.

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## Example 20

A linear polyamide was prepared by known methods from equimolar amounts of 1,11-diamino-3,6,9-trioxaundecane  $\text{NH}_2\text{—CH}_2\text{—CH}_2\text{—(OCH}_2\text{CH}_2)_3\text{NH}_2$  and sebacic acid dichloride

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by dissolving the two reactants in water and carbon tetrachloride respectively, and carrying out an interfacial polymerization.

20 10 g of purified polyamide dissolved in 100 ml of methylene chloride, 200 ml of  $\text{H}_2\text{O}$  and 0.3 g of cetylpyridinium bromide were homogenized to a drop size of 0.3—2  $\mu\text{m}$ . Methylene chloride was then removed by evaporation *in vacuo*.

25 10 ml of an aqueous dispersion containing 1.6 g of polyamide particles were treated with iron chloride and ammonia as described in example 1. In this case 1000 mg of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 350 mg of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were used.

The particles were separated from the solution by filtration, washed with water and finally with methanol. The particles were then dried. After the treatment the particles contain magnetic iron oxide. The iron content was found to be 11.5%.

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## Example 21

5.0 ml of dioctanoyl peroxide, 42.5 ml of  $\text{H}_2\text{O}$ , 7.5 ml of acetone and 0.15 g of Na-laurylsulphate were homogenized to an emulsion with a drop size of 0.2—0.4  $\mu\text{m}$ . This emulsion was combined with 23.1 ml of a latex consisting of monodisperse polystyrene particles having a diameter of 0.95  $\mu\text{m}$ . The amount of latex added contained 2.5 ml of polystyrene particles and 20.6 ml of  $\text{H}_2\text{O}$ . After careful stirring for 24 hours the acetone was evaporated *in vacuo*. The amount of latex after removal of the acetone was 71 ml.

A mixture of 52 ml of hydroxyethylmethacrylate, 78 ml of ethylene glycoldimethacrylate, 200 ml of cyclohexanol, 800 ml of water and 10 g of Pluronic F 68 (polyethylene oxide derivative) was emulsified with the ultraturrax mixer for 1 1/2 min. The emulsion was transferred to a reactor and the above latex residue of 71 ml was added. This mixture was stirred at a moderate rate for 2 hours. 800 ml of water was then added and the temperature was raised to 60°C. After the polymerization the reactor was cooled and cyclohexanol removed by several washings with water and isopropanol. After drying 125 g of monodisperse porous particles having a diameter of 4.0  $\mu\text{m}$  and a specific surface of 128  $\text{m}^2/\text{g}$  (BET) were obtained.

40 1.5 g of the dry particles were treated with a mixture of 25 ml of concentrated nitric acid and 65 ml of concentrated sulphuric acid with stirring for 1 hour. The mixture was then poured into a container containing 1 litre of ice. The particles were filtered off and washed until pH in the washings was neutral. After drying the particles were transferred to a rotating container together with 2.06 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  dissolved in 25 ml of water. The mixture was rotated for 30 minutes under an atmosphere of  $\text{N}_2$ . 10 ml of ammonia solution (25%) was then added by suction. The temperature was then raised to 80°C. After 15 minutes at 80°C the mixture was cooled and filtered. The particles were washed several times with water and methanol. After this treatment the particles contain magnetic iron oxide. The iron content in the particles was found to be 18.4%.

## Example 22

55 Monodisperse porous particles prepared as described in example 21 were used. The particles had a diameter of 4.0  $\mu\text{m}$  and a specific surface of 128  $\text{m}^2/\text{g}$ .

1 g of dry particles were added to 7.5 g  $\text{NaNO}_2$  dissolved in 15 ml of water under vigorous stirring with a magnetic stirrer. The mixture was then cooled to 0°C in an ice bath. For a period of 50 minutes 10 ml of concentrated hydrochloric acid were added dropwise. Then the mixture was heated to 20°C in 3 hours. The mixture was poured onto 40 g of ice and filtered. Washing was carried out with 1M Na-carbonate solution until the filtrate was neutral and then several times with water.

60 After drying 0.87 g of particles were added to a solution of 1 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  dissolved in 30 ml of water. The mixture was bubbled through with  $\text{N}_2$  (99.99%) and the mixture was rotated for 30 minutes under an atmosphere of  $\text{N}_2$ . Then 10 ml of ammonia solution (25%) was added by suction. Under a continued atmosphere of  $\text{N}_2$  the temperature was raised to 80°C. After 10 minutes at 80°C the mixture was

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cooled and filtered. After washing several times with water, the particles were dried at 60°C. After this treatment the particles contain magnetic iron oxide. The iron content in the particles was found to be 12.3%.

#### 5 Example 23

Monodisperse porous particles prepared as described in example 9 were used. The particles had a diameter of 4.8  $\mu\text{m}$  and a specific surface of 151  $\text{m}^2/\text{g}$ , and after treatment with ethylene diamine the particles contained 4.9% N.

1 g of dry particles was mixed with 834 mg of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (3 mmole) dissolved in 40 ml of water. The mixture was rotated for 30 minutes under an atmosphere of  $\text{N}_2$ . 10 ml of concentrated ammonia solution (25%) were then added by suction. The temperature was then raised to 80°C with a light suction of air through the apparatus. After 15 minutes at 80°C the mixture was cooled and the particles were washed several times with water and finally dried. After this treatment the particles contain magnetic iron oxide. The iron content in the particles was found to be 10.5%.

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#### Example 24

Monodisperse, porous polymer particles with amino groups were used, prepared as described in example 9. The particles had a diameter of 4.8  $\mu\text{m}$ , and after treatment with ethylene diamine the particles contained 4.9% N.

20 1 g of dry particles was added to 243 mg of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.92 mmole) dissolved in 15 ml of  $\text{H}_2\text{O}$  and 129 mg of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  (0.46 mmole) dissolved in 30 ml of  $\text{H}_2\text{O}$ . The mixture was rotated in a film evaporator at 25°C *in vacuo* for 10 minutes. Then the vacuum was eliminated and the rotation of the mixture was continued at 90°C for 15 minutes. 30 ml of 6N NaOH were then added. Heating was continued at 90°C for 1 hour. The particles were then cleaned by several washings with water and finally dried. After this treatment the particles contain a magnetic material. Analyses of the particles show a content of 4.4% Fe and 2.3% Co.

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#### Example 25

Monodisperse porous particles with nitro groups were used, prepared as described in example 12. The particles had a diameter of 2.0  $\mu\text{m}$  and after nitration they contained 8.8% N.

30 2 g of dry particles were added to 1.6 g of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (5.75 mmole) dissolved in 25 ml of  $\text{H}_2\text{O}$  and 0.8 g of  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  (2.84 mmole) dissolved in 40 ml  $\text{H}_2\text{O}$ . The mixture was rotated in a film evaporator at 25°C under an atmosphere of  $\text{N}_2$  for 30 minutes. 25 ml of 3N NaOH were then added and it was heated at 80°C for 1 hour under an atmosphere of  $\text{N}_2$ . After this treatment the particles contain a magnetic material. Analyses of the particles showed a content of 11.5% Fe and 6.1% Co.

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#### Example 26

Monodisperse polymer particles with amino groups were used, prepared as described in example 7. The particles had a diameter of 2.0  $\mu\text{m}$  and after treatment with ethylene diamine they contained 9.5% N.

40 1 g of dry particles was transferred to 20 ml of water, and 243 mg of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (0.92 mmole) dissolved in 15 ml of  $\text{H}_2\text{O}$  and 91 mg of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (0.46 mmole) dissolved in 15 ml of  $\text{H}_2\text{O}$  were added. The mixture was rotated in a film evaporator at 25°C *in vacuo* for 10 minutes. 20 ml of 3N NaOH were then added, and it was heated at 90°C for 1 hour under an atmosphere of  $\text{N}_2$ . The particles were then cleaned by washing several times with water and finally drying.

45 After this treatment the particles contain a magnetic material. Analyses of the particles showed a content of 4.3% Fe and 2.2% Mn.

#### Example 27

50 5 ml of dioctanoyl peroxide, 42.5 ml of  $\text{H}_2\text{O}$ , 7.5 ml of acetone and 0.15 g of Na-laurylsulphate were homogenized to an emulsion with a drop size of 0.2—0.4  $\mu\text{m}$ . This emulsion was combined with 28 ml of a latex consisting of monodisperse polystyrene particles having a diameter of 2.0  $\mu\text{m}$ . The amount of latex added contained 2.27 ml of polystyrene particles and 25.73 ml of  $\text{H}_2\text{O}$ .

After careful stirring of this mixture for 24 hours all the dioctanoyl peroxide added were taken up in the polystyrene particles. Acetone was then removed by evaporation *in vacuo*, and there was obtained a residue of 75.5 ml of latex containing 7.27 ml of polystyrene-dioctanoyl peroxide particles. A mixture of 800 ml of water, 0.6 g of Na-laurylsulphate, 12 g of polyvinylpyrrolidone (MW 360 000), 60 ml of ethylacrylate, 90 ml of divinyl benzene (50%) and 150 ml of cyclohexanol was homogenized by means of an ultraturrax mixer. The mixture was transferred to a reactor, and the above latex of 75.5 ml was then added. The reactor was then closed and stirring was continued at 25°C for 20 hours. Then 800 ml of  $\text{H}_2\text{O}$  were added, and the reactor was heated to 60°C. Polymerization was carried out for 2 hours at 60°C and then for 5 hours at 70°C until the reaction was complete. After washing the product with water and isopropanol, filtration and drying there was obtained a powder consisting of monodisperse macroporous polymer particles having a diameter of 9.8  $\mu\text{m}$ .

60 5 g of dry particles were mixed with 50 ml of diethylenetriamine in a small three-necked flask fitted with stirrer and a short fractionating column. The temperature was gradually raised to 200°C. The heating was continued for 5 hours. Ethyl alcohol distilled off through the column. After dilution with water the particles

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were purified by filtration and several times washing with water and finally drying. Elementary analysis showed that the particles contained 3.2% N.

2 g of the particles were transferred to 20 ml of water and treated with iron chloride and ammonia solution as described in example 1. In this case 690 mg (2.55 mmole)  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  in 25 ml of water and 288 mg (1.45 mmole) of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  in 25 ml of water were used, and 20 ml of ammonia solution (25%) were added.

After the treatment was brought to an end, the particles were filtered from the solution and washed with water and finally with methanol. The particles were then dried. After this treatment the particles contain magnetic iron oxide. The iron content was found to be 9.5%.

## Claims

1. Process for the preparation of magnetic polymer particles, characterized in that solutions of iron salts and optionally salts of other metals which are capable of forming magnetic ferrites, in water or in a mixture of water and water-soluble organic solvents or in organic solvents, are mixed with polymer particles in dry form or dispersed in water or in a mixture of water and water-soluble organic liquids or in organic liquids, and the metals are precipitated in the form of hydroxides, and, optionally, the particles are heated.
2. Process according to claim 1, characterised by using
  - a) polymer particles which contain groups which may bind metal salts so that the essential part of the metal salts added are bound on and/or in the particles, whereafter pH is increased, and when a suitable mixture of 2-valent iron salt and/or other metal salts and of 3-valent iron salt is used, a mixture of  $\text{Me}(\text{OH})_2$  [ $\text{Me}=\text{Fe}^{\text{II}}$ , Ni, Co, Mn] and  $\text{Fe}(\text{OH})_3$  is obtained which provides magnetic material on and in the particles, and if a higher amount than desired of 2-valent is present in the salt formed, it is oxidized after raising the pH, to form a mixture of  $\text{Me}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$  which provides magnetic material on and in the particles,
  - b) polymer particles which contain groups having the ability to oxidize  $\text{Fe}(\text{OH})_2$  entirely or partly to  $\text{Fe}(\text{OH})_3$ , so that the 2-valent iron salt and possible other metal salts added are bound in the particles upon a raise in the pH value and are converted to magnetic material,
  - c) polymer particles which are cross-linked, and to these there is added a possibly aqueous organic solvent containing a metal salt with hydrophobic anions which is soluble in said solvent, whereby the particles absorb said solvent so that the metal salts are incorporated in the particles, whereafter the particles are isolated, and water is added and pH raised to form a mixture of  $\text{Me}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$  which, if desired, after oxidation as in a), provides magnetic material,
  - d) solid, porous polymer particles to which there is added a material which will attach to the surface of the pores and which contains groups which bind the metal salt which is added.
3. Process according to claims 1 or 2, characterized in that the polymer particles are prepared by copolymerization of vinyl monomer with epoxy groups and other vinyl monomers and/or polyvinyl monomers, and are then treated with substances containing one or more primary and/or secondary amino groups which react with the epoxy group so that these substances are bound on and in the particles and provide groups which are capable of binding metal salts with coordinate bonding.
4. Process according to claims 1 or 2, characterized by copolymerization of a mixture of vinyl monomers and, if desired, polyvinyl monomers, in which one or more of the monomers contain amino groups to form directly polymer particles containing amino groups which upon addition of a mixture of metal salts bind these on and in the particles, or in which one or more of the monomers contain acid groups or groups which may be converted to acid groups, such as ester groups, which have the effect that the polymer particles formed contain acid groups which in ion form may bind metal salts by ionic bonds.
5. Process according to claims 1 or 2, characterized in that to obtain metal-binding primary and/or secondary and/or tertiary amino groups or acid groups on the interior surface of porous particles, there are added substances which are bound to the surface by physical absorption and which contain said groups which will bind metal ions so that the metal ions are bound in and on the particles upon the subsequent addition of metal salt.
6. Process according to claims 1 or 2, characterized by using porous particles prepared by copolymerization of a mixture of styrene, styrene derivatives or acrylates and divinyl benzene or di- or triacrylates in the presence of inert additives.
7. Process according to any of claims 1, 2 and 6, characterized by using polymer particles containing nitrogen oxide groups such as  $\text{NO}_2$ ,  $\text{ONO}_2$  or  $\text{ONO}$ .
8. Process according to any of claims 1, 2, 3 and 6, characterized in that amino groups and/or imino groups, or ethylene oxide groups are incorporated in the ready polymerized particles.
9. Process according to any of claims 1, 2 and 6, characterized in that acid groups, particularly sulphonic acid or carboxylic acid groups are incorporated in the ready polymerized particles.
10. Process according to any of claims 1 to 9 characterised by using monodisperse polymer particles.

## Patentansprüche

1. Verfahren zur Herstellung von magnetischen Polymerteilchen, dadurch gekennzeichnet, daß

Lösungen von Eisensalzen, und gegebenenfalls Salzen anderer Metalle, welche magnetische Ferrite zu binden vermögen, in Wasser oder in einem Gemisch von Wasser und wasserlöslichen organischen Lösungsmitteln oder in organischen Lösungsmitteln mit Polymerteilchen in trockener Form, oder dispergiert in Wasser oder in einem Gemisch von Wasser und wasserlöslichen organischen Flüssigkeiten oder in organischen Flüssigkeiten vermischt werden, und die Metalle in Form von Hydroxiden gefällt werden, und die Teilchen gegebenenfalls erhitzt werden.

2. Verfahren gemäß Anspruch 1, gekennzeichnet durch die Verwendung von

a) Polymerteilchen, welche Gruppen enthalten, die Metallsalze binden können, so daß der wesentliche Teil der zugesetzten Metallsalze auf und/oder in den Teilchen gebunden wird, wonach das pH erhöht wird, und wenn eine geeignete Mischung von zweiwertigem Eisensalz und/oder anderen Metallsalzen und von dreiwertigem Eisensalz verwendet wird, ein Gemisch von  $\text{Me}(\text{OH})_2$  [ $\text{Me}=\text{Fe}^{\text{II}}$ , Ni, Co, Mn] und  $\text{Fe}(\text{OH})_3$  erhalten wird, welches magnetisches Material auf und in den Teilchen schafft, und wenn eine höhere Menge als gewünscht an zweiwertigem Eisen in dem gebildeten Salz vorhanden ist, wird es nach Ansteigen des pHs oxidiert, um ein Gemisch von  $\text{Me}(\text{OH})_2$  und  $\text{Fe}(\text{OH})_3$  zu bilden, welches magnetisches Material auf und in den Teilchen schafft,

b) Polymerteilchen, welche Gruppen enthalten, die die Fähigkeit haben,  $\text{Fe}(\text{OH})_2$  gänzlich oder teilweise zu  $\text{Fe}(\text{OH})_3$  zu oxidieren, so daß das zugesetzte zweiwertige Eisensalz und gegebenenfalls andere Metallsalze in den Teilchen nach Ansteigen des pH-Werts gebunden und zu magnetischem Material umgewandelt werden,

c) Polymerteilchen, welche vernetzt sind und zu diesen ein gegebenenfalls wäßriges organisches Lösungsmittel gegeben wird, das ein Metallsalz mit hydrophoben Anionen enthält, das in diesem Lösungsmittel löslich ist, wodurch die Teilchen dieses Lösungsmittel absorbieren, so daß die Metallsalze in die Teilchen einverleibt werden, wonach die Teilchen isoliert werden und Wasser zugesetzt und das pH erhöht wird, um ein Gemisch von  $\text{Me}(\text{OH})_2$  und  $\text{Fe}(\text{OH})_3$  zu bilden, das gewünschtenfalls nach Oxidation wie in a) magnetisches Material schafft,

d) feste, poröse Polymerteilchen, denen ein Material zugesetzt wird, welches sich an der Oberfläche der Poren verknüpft und das Gruppen enthält, die das Metallsalz, das zugesetzt wurde, binden.

3. Verfahren gemäß den Ansprüchen 1 oder 2, dadurch gekennzeichnet, daß die Polymerteilchen hergestellt werden durch Copolymerisation von Vinylmonomerem mit Epoxygruppen und anderen Vinylmonomeren und/oder Polyvinylmonomeren und dann mit Substanzen behandelt werden, welche eine oder mehr primäre und/oder sekundäre Aminogruppen enthalten, die mit der Epoxygruppe reagieren, so daß diese Substanzen auf und in den Teilchen gebunden werden und Gruppen schaffen, welche zur Bindung von Metallsalzen mit koordinierter Bindung fähig sind.

4. Verfahren gemäß den Ansprüchen 1 oder 2, gekennzeichnet durch die Copolymerisation eines Gemisches von Vinylmonomeren und gewünschtenfalls Polyvinylmonomeren, worin ein oder mehrere der Monomeren Aminogruppen enthalten, um direkt Aminogruppenhaltige Polymerteilchen zu bilden, welche nach Zugabe eines Gemisches von Metallsalzen diese auf und in den Teilchen binden, oder worin ein oder mehrere der Monomeren Säuregruppen oder Gruppen, die in Säuregruppen überführt werden können, wie Estergruppen, enthalten, welche die Wirkung haben, daß die gebildeten Polymerteilchen Säuregruppen enthalten, welche in Ionenform Metallsalze durch ionische Bindungen binden können.

5. Verfahren gemäß den Ansprüchen 1 oder 2, dadurch gekennzeichnet, daß zur Erzielung von metallbindenden primären und/oder sekundären und/oder tertiären Aminogruppen oder Säuregruppen auf der inneren Oberfläche von porösen Teilchen Substanzen zugesetzt werden, welche an die Oberfläche durch physikalische Absorption gebunden sind, und welche diese Gruppen, welche Metallionen binden werden, enthalten, so daß die Metallionen in und auf den Teilchen nach anschließender Zugabe des Metallsalzes gebunden werden.

6. Verfahren nach den Ansprüchen 1 oder 2, dadurch gekennzeichnet, daß poröse Teilchen verwendet werden, welche durch Copolymerisation eines Gemisches von Styrol, Styrolderivaten oder Acrylaten und Divinylbenzol oder Di- oder Triacrylaten in Anwesenheit von inerten Zusätzen hergestellt sind.

7. Verfahren gemäß einem der Ansprüche 1, 2 und 6, dadurch gekennzeichnet, daß Polymerteilchen, welche Stickstoffoxidgruppen wie  $\text{NO}_2$ ,  $\text{ONO}_2$  oder  $\text{ONO}$  enthalten, verwendet werden.

8. Verfahren nach einem der Ansprüche 1, 2, 3 und 6, dadurch gekennzeichnet, daß Aminogruppen und/oder Iminogruppen, oder Ethylenoxidgruppen in den fertigen polymerisierten Teilchen einverleibt werden.

9. Verfahren nach einem der Ansprüche 1, 2 und 6, dadurch gekennzeichnet, daß Säuregruppen, insbesondere Sulfonsäure- oder Carbonsäuregruppen, in die fertigen polymerisierten Teilchen einverleibt werden.

10. Verfahren gemäß einem der Ansprüche 1 bis 9, dadurch gekennzeichnet, daß monodisperse Polymerteilchen verwendet werden.

## Revendications

1. Procédé pour la préparation de particules polymères magnétiques, caractérisé par le fait que des solutions de sels de fer et éventuellement de sels d'autres métaux qui sont capables de former des ferrites magnétiques, dans de l'eau ou dans un mélange d'eau et de solvants organiques solubles dans l'eau, ou



dans des solvants organiques, sont mélangées avec des particules polymères à l'état sec ou dispersées dans de l'eau ou dans un mélange d'eau et de liquides organiques solubles dans l'eau, ou dans des liquides organiques, et que les métaux sont précipités sous forme d'hydroxydes, et que les particules sont éventuellement chauffées.

5 2. Procédé selon la revendication 1, caractérisé par l'utilisation

a) de particules polymères qui contiennent des groupes qui peuvent fixer des sels métalliques si bien que la majeure partie des sels métalliques ajoutés est fixée sur et/ou dans les particules, après quoi on augmente le pH et, lorsque l'on utilise un mélange approprié de sel de fer bivalent et/ou d'autres sels métalliques et de sel de fer trivalent, on obtient un mélange de  $\text{Me}(\text{OH})_2$  ( $\text{Me}=\text{Fe}^{\text{II}}$ , Ni, Co, Mn) et de  $\text{Fe}(\text{OH})_3$  qui fournit un produit magnétique sur et dans les particules, et si une quantité de fer bivalent plus élevée qu'on le souhaite est présente dans le sel formé, elle est oxydée après l'augmentation du pH, pour former un mélange de  $\text{Me}(\text{OH})_2$  et de  $\text{Fe}(\text{OH})_3$  qui fournit un produit magnétique sur et dans les particules,

10 b) de particules polymères qui contiennent des groupes ayant la capacité d'oxyder complètement ou partiellement  $\text{Fe}(\text{OH})_2$  en  $\text{Fe}(\text{OH})_3$ , si bien que le sel de fer bivalent et éventuellement d'autres sels métalliques ajoutés sont fixés sur les particules lorsque l'on augmente la valeur du pH et sont transformés en produit magnétique,

c) de particules polymères qui sont réticulées, et l'on ajoute à celles-ci un solvant organique éventuellement aqueux contenant un sel métallique avec des anions hydrophobes qui est soluble dans ledit solvant, ce par quoi les particules absorbent ledit solvant, si bien que les sels métalliques sont 20 incorporés dans les particules, après quoi les particules sont isolées, puis on ajoute de l'eau et on élève le pH pour former un mélange de  $\text{Me}(\text{OH})_2$  et de  $\text{Fe}(\text{OH})_3$  qui, si on le désire, après oxydation comme en a), fournit un produit magnétique,

d) de particules polymères poreuses, solides, auxquelles est ajoutée une substance qui se fixe à la surface des pores et qui contient des groupes qui fixent le sel métallique qui est ajouté.

25 3. Procédé selon les revendications 1 ou 2, caractérisé par le fait que les particules polymères sont préparées par copolymérisation de monomère vinylique avec des groupes époxy et d'autres monomères vinyliques et/ou de monomères polyvinyliques, et qu'elles sont traitées ensuite avec des substances contenant un ou plusieurs groupes amino primaires et/ou secondaires qui réagissent avec le groupe époxy si bien que ces substances sont fixées sur et dans les particules et fournissent des groupes qui sont 30 capables de fixer des sels métalliques par liaison coordonnée.

4. Procédé selon les revendications 1 ou 2, caractérisé par la copolymérisation d'un mélange de monomères vinyliques et, si on le désire, de monomères polyvinyliques, dans lequel un ou plusieurs des monomères contiennent des groupes amino pour former directement des particules polymères contenant des groupes amino qui, lors de l'addition d'un mélange de sels métalliques, fixent ceux-ci sur et dans les 35 particules, ou dans lequel un ou plusieurs des monomères contiennent des groupes acides ou des groupes qui peuvent être transformés en groupes acides, tels que des groupes esters, ce qui a pour effet que les particules polymères formées contiennent des groupes acides qui, sous forme ionique, peuvent fixer des sels métalliques par des liaisons ioniques.

5. Procédé selon les revendications 1 ou 2, caractérisé par le fait que, pour obtenir sur la surface interne 40 de particules poreuses des groupes amino primaires et/ou secondaires et/ou tertiaires ou des groupes acides, fixant des métaux, on ajoute des substances qui sont fixées à la surface par absorption physique et qui contiennent lesdits groupes qui fixent des ions métalliques, si bien que les ions métalliques sont fixés dans et sur les particules lors de l'addition subséquente de sel métallique.

6. Procédé selon les revendications 1 ou 2, caractérisé par l'utilisation de particules poreuses préparées 45 par copolymérisation d'un mélange de styrène, de dérivés de styrène ou d'acrylates et de divinylbenzène ou de di- ou tri-acrylates en présence d'additifs inertes.

7. Procédé selon l'une quelconque des revendications 1, 2 et 6, caractérisé par l'utilisation de particules polymères contenant des groupes oxyde d'azote tels que  $\text{NO}_2$ ,  $\text{ONO}_2$  ou  $\text{ONO}$ .

8. Procédé selon l'une quelconque des revendications 1, 2, 3 et 6, caractérisé par le fait que des groupes 50 amino et/ou des groupes imino, ou des groupes éthylène-oxyde sont incorporés dans les particules déjà polymérisées.

9. Procédé selon l'une quelconque des revendications 1, 2 et 6, caractérisé par le fait que des groupes acides, en particulier des groupes acide sulfonique ou acide carboxylique sont incorporés dans les particules déjà polymérisées.

55 10. Procédé selon l'une quelconque des revendications 1 à 9, caractérisé par l'utilisation de particules polymères monodispersées.